

NAS president Frank Press
calls on science community to
set its own priorities Page 27

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CHEMICAL & ENGINEERING

NEWS

Plastics Additives

New products provide improved
properties and processing
Page 35

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News of the Week

■ Methyl isocyanate gas may have wider ranging systemic effects than previously thought. **Page 6**

■ The 3rd Chemical Congress of North America attracted over 14,000 to Toronto last week. **Page 7**

■ Researchers have confirmed that an oncogenic protein can directly control other genes. **Page 8**

■ X-ray crystallographic studies reveal how new antiviral compounds bind to viruses. **Page 8**

■ A new computer journal for organic chemists is being published by Pergamon Press. **Page 8**

■ Concern grows about damage to U.S. space program from ammonium perchlorate shortages. **Page 9**

■ The governors of New York and Ohio have agreed on a formula to limit acid rain emissions. **Page 9**

■ OSHA is proposing a toughening of permissible exposure levels for 234 chemicals. **Page 10**

Cover: Ethyl Corp. supplies brominated flame retardants for plastics from this Arkansas facility

Letters 4

Concentrates

Business 11

Government 16

Science/Technology 22

The Departments

New Products 53

Awards 61

Newsclips 76

Business

Emerging chemical trade in developing nations in Far East, Pacific Rim, other regions will present new challenge for industry, Shell executive predicts. **Page 14**

Government

Presidential contenders Bush, Dukakis, Jackson hold similar positions on domestic and global environmental issues. **Page 17**

Science Policy

NAS president Frank Press discusses need for science to set its own priorities, some key science and technology issues. **Page 27**

Technology

New type of LC/MS interface makes it possible to identify compounds not amenable to GC/MS determination. **Page 31**

Yale scientists are using electrospray ionization MS to determine high molecular weight proteins on a quadrupole analyzer with an upper mass limit of only 1600 daltons. **Page 32**

Education

ACS has published a sourcebook aimed at enlivening the content of undergraduate physical chemistry courses. **Page 34**

Books

"Petrochemicals: The Rise of an Industry" by Peter H. Spitz is an optimistic look at an industry with a dramatic past. **Page 58**



Product Report

Amount of additives used in plastics is declining as products that provide the same or improved performance at lower concentrations become increasingly available. **Page 35**

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LETTERS

CHEMICAL SAFETY

Di-tert-butyl peroxide

SIR: In the course of carrying out a routine undergraduate physical chemistry laboratory experiment, a violent explosion occurred. The experimental procedure was nearly identical to that described in the literature [Trotman-Dickenson, A. F., *J. Chem. Ed.*, **46**, 396 (1969)] for the gas-phase decomposition of di-tert-butyl peroxide. Our apparatus utilized a mercury manometer rather than a Bourdon gauge, but otherwise was identical to that of Trotman-Dickenson. In the past two years, our physical chemistry laboratory students have performed the experiment between 20 and 30 times with excellent results and no hint of danger.

On Thursday morning, April 14, 1988, a student completed his first run at 155 °C with normal results, according to his notes. A second run was initiated by injecting 0.2 mL of di-tert-butyl peroxide through a rubber septum into a 250 mL reaction flask at 165 °C. The student read the initial pressure on the manometer, turned his back to the apparatus,

took three steps to his notebook to record his data, and the explosion occurred. Standing in my adjoining office about 12 meters away, I whirled around in time to see an orange fire ball floating toward the ceiling. The explosion blew hot oil, thermostating the reaction vessel upwards toward the ceiling. A few drops fell upon the student causing minor burns on the back of his neck.

Although only 0.2 mL of di-tert-butyl peroxide was used, the explosion was violent and frightening to others in the room and to myself. The report was at least as loud as a 12-gauge shotgun. No errors on the part of the student were evident. If contamination was a contributing cause, it was not of the kind that could reasonably be controlled in an undergraduate laboratory situation. Consequently, we are discontinuing this experiment and would advise other users of di-tert-butyl peroxide in similar situations to do likewise.

Rodney J. Sime

Department of Chemistry
California State University, Sacramento

News on dioxin

SIR: Did I miss it? Or have you failed to note in your columns the important new report from the Air Force on agent orange ("United States Air Force Personnel and Exposure to Herbicide Orange" by Richard A. Albanese, M.D., Feb. 1988, USAFSAM-TR-88-3, available from USAF School of Aerospace Medicine, Human Systems Division, Brooks Air Force Base, Tex. 78235-5301), which indicates that Air Force personnel exposed to agent orange in Vietnam have suffered major health damage compared to those not exposed? The health damage includes a significant increase in the incidence of cancer, liver damage, cardiovascular disease, birth defects, and psychological change.

This report reverses findings of previous Ranch Hand studies (which received wide publicity in your journal and elsewhere) that indicated that there was no significant difference between those exposed and those unexposed.

Although Albanese's study is not definitive proof that dioxin is the causative agent for this human health damage, it should surely put an end to those complacent statements from so many government and industrial spokesmen who tell the public that while dioxin is in-

credibly toxic for a wide range of animal species, it appears to do little damage to human beings.

The wary should have been suspicious of humans being the beneficiary of such a biochemical miracle, especially when no mechanism was ever offered that would explain how humans escape dioxin's attentions.

Meanwhile, for those who wish to see the matter finally proved (one way or the other) it is critical that the government agencies investigating dioxin ex-

Correction

• May 16, page 14: In the pharmaceutical companies table, Abbott Labs' sales were \$1.188 billion, not \$219.3 million; earnings, \$172.1 million, not \$8.4 million, in the first quarter. Sales and earnings were up 18% and 22%, respectively, not 9% and 13%, in the first quarter; profit margins were 14.5%, not 3.8%, in the first quarter, and 14.1%, not 3.7%, in the year-earlier quarter. Bristol-Myers' after-tax earnings in first-quarter 1988 were up 21%, not down 25%, and its profit margin in 1987 was 12.9%, not 13.9%.

The diskette material will enable the reader to repeat demonstrations described in the paper, apply programs to his or her own work, and verify at once that the techniques perform as the author claims. Referees also will be able to review papers by actual use. Diskettes can be run on IBM PC and PS/2 or compatible microcomputers.

The new journal will publish papers, communications, reviews of research topics and of software, and news items. Papers will appear in as little as 90 days after submission, says organic chemistry professor Todd W. Wipke of the University of California, Santa Cruz, who will edit the journal.

Such rapid publication plus acceptance of communications that are shorter than full papers will let chemists see and use the work of others sooner than is now possible Wipke says. Too, chemists whose work is published in preliminary

communications will be credited with inventing their techniques. At present, it often takes three years of work before results of a project are published.

Such rapid publication will be possible for papers submitted electronically as ChemText files, Wipke says. ChemText is a word and graphics processor that allows inclusion of texts and graphics in the same document. The program is published by Molecular Design, San Leandro, Calif., of which Wipke is a vice president.

Authors also may submit papers as typed manuscripts or electronically in a standardized format called ASCII. Institutional subscription prices will be \$375 for the three issues of 1988, \$750 for the six issues of 1989, or \$750 for all nine issues of 1988 and 1989 if ordered all at once. Individual subscriptions will be \$75.

Stephen Stinson, New York

Concern rises over rocket oxidizer supply

The U.S. may be facing a crisis in its space and missile programs over the next three years because of shortages of the solid fuel oxidizer ammonium perchlorate, warn members of Congress. But officials from the Department of Defense and National Aeronautics & Space Administration told a hearing last week that proper allocations, shifts and delays in programs, and building of new capacity should enable the nation to avoid any serious crisis.

"This country is on the brink of a national emergency," said Rep. Rob-

ert A. Roe (D.-N.J.), chairman of the House Science Space & Technology Committee and of its Investigations & Oversight Subcommittee. Roe was referring to the explosion early last month in Henderson, Nev., which leveled a Pacific Engineering & Production Co. plant, one of only two U.S. plants producing ammonium perchlorate (C&EN, May 16, page 5).

The plant was making 20 million lb a year of the perchlorate and had a capacity of up to 40 million lb. It was the principal supplier to the space shuttle program, and sole supplier for the Titan rocket and several military missiles.

The explosion killed two workers, injured hundreds of local residents, and destroyed much property in Henderson. Under local pressure, Kerr-McGee Chemical Corp. has shut down its perchlorate plant, also sited in Henderson, for safety checks most of the past month, idling its 36 million lb-a-year capacity. Local leaders have threatened suits to keep it closed.

A recovery strategy is being formed by an interagency group, with members from DOD and NASA

and liaison with the departments of Commerce and Transportation. Detailed plans for rebuilding capacity, and for allocating production in the meantime, will be ready later this month.

The first step in recovery is to restart Kerr-McGee's production, and at press time the plant planned to reopen on June 13. Its capacity is also to be raised to 40 million lb a year. Then, with federal aid, Kerr-McGee and Pacific will build new plants with 20 million lb and 30 million lb annual capacities, respectively, but not in Henderson. NASA and DOD expect construction and qualifying to meet federal requirements to take about a year.

The interagency group expects that if all goes according to plan, all 1988 needs (38.8 million lb) can be satisfied, although schedules may be stretched out. And if expansion plans go ahead, it believes the shortfall in 1989 can be reduced to 3 million lb out of a demand of 60 million. Allocation plans will look at such steps as shifting some payloads from the shuttle (1.7 million lb of ammonium perchlorate per launch) to unmanned Titan IV rockets (800,000 lb per launch).

Subcommittee members were very skeptical of these projections, and will further question the plans at a hearing in a few weeks. "Let's not dance around it," says Roe. "We're in trouble."

Richard Seltzer, Washington

Ohio, New York agree on acid rain proposal

In a maneuver to break the Congressional deadlock over legislation to control acid rain, the governors of Ohio and New York have agreed on a formula to limit sulfur dioxide emissions from the combustion of coal, and nitrogen oxides from coal and other sources. Their proposal would come in the form of amendments to the Clean Air Act and could possibly speed acid rain legislation this year.

The agreement was about a year in the making and was signed by governors Mario M. Cuomo of New York and Richard F. Celeste of Ohio,

Ammonium perchlorate use in rockets to soar

Millions of lb	1988	1989	1990
Army	9.3	14.0	11.7
Navy	3.7	6.5	5.4
Air Force	11.0	11.5	16.1
NASA	6.5	19.6	22.1
Commercial space launchers	3.5	3.7	5.2
EMLRs*	1.8	2.6	5.3
Other export	1.0	2.0	2.0
TOTAL	38.8	60.1	67.8

* European Multiple-Launch Rocket System. Source: Department of Defense

Plastics Additives: Less Performing Better

Bruce F. Greek, C&EN Houston

Plastics additives, a complex and growing group of minerals and chemical derivatives, go into such a diversity of products that their outlook is hard to assess. Growth in use of additives, which often impart more than one property to resins, is lagging growth of plastics because of the increasing availability of additives that will provide the same or improved performance at lower concentrations. Demand for additives, however, is strong enough to spur many producers to expend money and effort to expand their lines and to build new capacity.

New additives for plastics continually come to market. They, along with existing ones, go into plastics at average rates slightly lower than in the past. The lower unit consumption results from constant improvement in the additives offered and improved plastics processing technology. Despite lower application rates, plastic products are fabricated with more processing ease and are increasingly well accepted by consumers. A significant concern about additives is their impact on the environment, particularly the

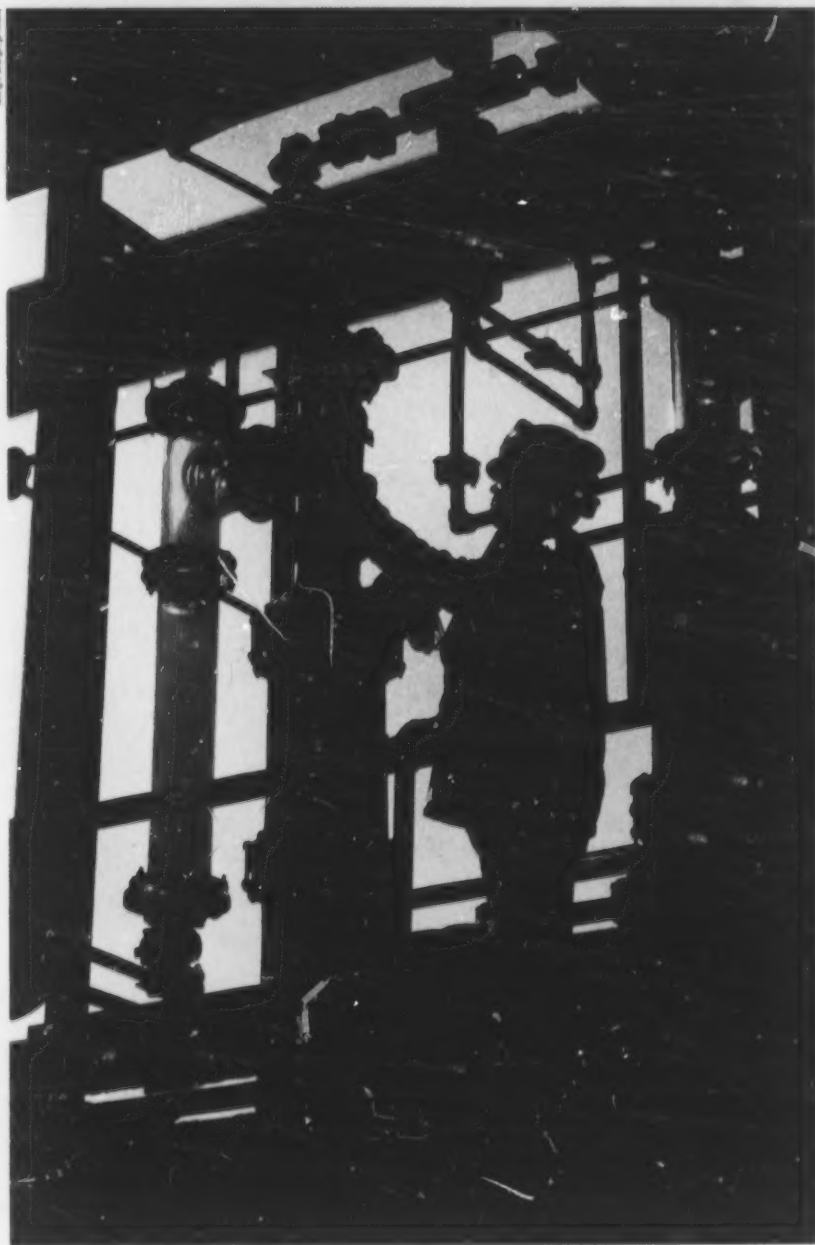
disposal of additives that are in discarded plastic items and the health and safety of workers exposed to the additives during fabrication of the plastic products.

This year, about 10 billion lb of additives will go into more than 50 billion lb of plastic resins before the fabricated products reach the consumer, according to industry sources. No complete tabulation of the different additives used in plastics is available, but indications are that more than 4000 individual products exist. Many additives used in plastics also go into other consumer products, such as rubber, paints, and textiles. The use of additives in plas-

tics is sometimes referred to as a "black art," because compounders rely on their own expertise in the application of additives to achieve desired properties and performance of the fabricated plastic item, sometimes quite without solid technical rationale. As a result, precise data on consumption of additives in plastics are not likely to become available. Most estimates are based on assumptions of an average use of functional classes of additives.

Three functional classes of additives—fillers, plasticizers, and reinforcements—account for about 85% of all additives used in plastics, estimates Freedonia Group, a Clevel-

Ethyl Corp. photo



Several additives may be used in single plastic resin

	Antioxidant	Antistat	Catalyst	Flame retardant	Heat stabilizer	Impact modifier	Initiator	Lubricant & mold release	Plasticizer	Preservative	UV stabilizer
ABS	●	●		●		●	●	●			●
Acrylic		●		●		●	●	●	●		●
Epoxy				●				●			●
Nylon	●	●	●								
Phenolic				●				●			
Polycarbonate		●	●	●		●					
Polyester, unsaturated	●	●		●			●	●			●
Polyethylene, high density	●	●	●	●		●		●		●	●
Polyethylene, low & linear low density	●	●	●	●		●		●		●	●
Polypropylene	●	●	●	●		●		●			●
Polystyrene	●	●		●		●	●	●	●		●
Polyurethane		●		●						●	
Polyvinyl acetate		●		●	●		●		●		
Polyvinyl chloride	●	●		●	●	●	●	●	●	●	●
Thermoplastic polyester		●	●			●		●			

Note: Additives used in many of above plastics, but not indicated, include solvents, molecular weight controls, emulsifiers, blowing agents, fillers and reinforcements, colorants, and coupling agents.

land-based business database research firm. Those classes of materials, relative to resins, generally are chemically inert. Except for plasticizers, they also are unaffected by light, heat, and atmosphere. Another functional class, colorants (which accounts for about 4.5% of the additives used), also does not react with most resins.

The remaining 10% of plastics additives—the chemically reactive products—is dominated by flame retardants. Chemically reactive products also are used in plastics resins to impart longer life or improved performance to the fabricated products, to improve processibility of resins during fabrication, or to permit forms not otherwise easily attained without the additive. Another functional class of additives—the antistatic agents—gives ease in handling.

The outlook for use of plastics

additives varies with the class of the material. The overall growth in demand for additives, of course, is linked to that of fabricated plastic products. And growth of plastic products will depend on how well they provide less costly or better substitutes for other materials through advances in polymer production and processing technology. The market for plastics additives, as a whole, will grow 3.5% to 4.0% annually over the next few years, industry sources forecast.

Use of some of the small-volume, chemically reactive plastics additives will grow faster than that for all plastics additives, according to Freedonia Group. Ultraviolet stabilizers, impact modifiers, and antistatic agents are examples of the faster growing groups of additives. Improvements in quality of these additives is an important factor in the higher growth rates. Better pro-

cessing machinery and techniques also are fostering their use.

Government laws and regulations are both helping and hindering the growth of plastics additives. The increased requirements for flame retardancy in plastic building and construction products are spurring the use of flame retardant additives. But concern over the environmental impact of the additives (as well as resins) and concern for worker exposure during processing and fabrication of plastics where additives are involved are dampening the use of additives.

Plastics additives enter the environment via various routes, according to a study carried out by Radian Corp. for the Environmental Protection Agency and published by Noyes Data Corp., Park Ridge, N.J. During processing, additives may form volatiles (including aerosols) and particulates. Contact of those chemicals with water can lead to leaching and subsequently to possible contamination of water supplies. Volatiles and water contamination present potential problems when plastic products are burned or dumped in a landfill.

However, the environmental impact of additives in plastics is not always clear-cut, according to the Radian study. For example, many additives—such as colorants and fillers—are selected because they will remain in plastic resins. Others, such as phthalate plasticizers, exude from fabricated plastic products or are extracted by water or other solvents even if removal is not wanted or intended.

Plastic food packaging that contains additives must meet Food & Drug Administration guidelines, and the list of additives permitted for these uses is relatively short. These additives have low toxicity or are materials "generally recognized as safe" because experience has shown them to be so. Other additives that go into such plastic products as pipe, toys, furniture, and housewares are selected to limit the danger of exposure to them upon intentional or accidental contact.

The Radian report points out, however, that additives are but part of the impact of plastic products on the environment. Other factors in-

Additives vital to broad array of plastics

Additives improve the processing and performance of plastics and often have overlapping functional activities. Additives can be divided into four major areas of use, with each area containing subgroups of compounds having a particular functional activity. In these subgroups, a few compounds dominate use. However, many compounds may be used to obtain a particular function. Many other types of functional activity are obtained by additives not included in this list.

REACTION CONTROLS

Numerous chemicals used to control polymerization and other reactions overlap in their functions. Some are not true additives in that frequently they are absent in the fabricated products. If they are present in the final plastic products, they seldom have more than a minor effect on properties.

Catalysts are used in various ways in the polymerization process to make plastics. They differ from initiators in that they are not consumed, and, in the case of thermoplastics, generally do not become part of the polymers. Some catalysts are removed after polymerization. Hence, technically, they are not plastics additives. Others are left in the plastics because they have no significant effect on desired properties and because the cost of removal can be high.

Numerous catalysts now are used in making plastics, and the patent literature abounds with many more possibilities. Typical examples of catalysts used to make polyolefins (the various polyethylenes and polypropylenes) are metal oxides and the Ziegler-Natta systems containing aluminum alkyls and transi-

tion metal salts. Examples of catalysts to make thermosets (such as phenolics) are various acids and bases. Combinations of complex amines and organometallics (most often tin compounds) are examples of catalysts used in urethanes.

Initiators often replace or aid catalysts in polymerizations to produce polyvinyl chloride, the various styrenics, and other plastics. Peroxides—dialkyl, diacyl, and hydro—make up the largest share of initiators used commercially. Because initiators decompose to provide free radicals for reactive sites, their decomposition products become additives in plastics and may or may not be removed later.

Auxiliary processing materials frequently are tailored to specific polymerization processes and may be necessary to obtain the desired properties in a particular plastic. There are many examples of these materials, and they may be used in making just one or many polymers. Whether these materials or their decomposition products remain in the plastics depends on their usefulness and on subsequent processing of the plastics.

Solvents, one example of these auxiliaries, are widely used in making thermoplastics and are almost totally removed. Molecular weights of plastics are controlled by chain transfer agents, such as thiols; chain terminators, such as hydrogen and simple hydrocarbons; and crosslinking agents, such as divinylbenzene. Other auxiliaries are chemicals to control solution pH. Primary emulsifiers and secondary emulsifiers (protective gels) are required for emulsion and suspension polymerizations.

PROCESSING ADDITIVES

Various chemicals have been found to help processors make specialized forms of plastics. These chemicals also may speed processing.

Blowing agents are used to make foamed plastics. Polyurethanes account for more than two thirds of foamed plastics production. Physical blowing agents (about 90% of consumption) are liquefied gases such as chlorofluorocarbons (CFCs) and propane. (The continuing use of blowing agents that contain CFCs is in some doubt because of the current concern over ozone depletion.) Chemical blowing agents largely are complex derivatives of hydrazine. Many other chemicals, such as catalysts, surfactants, and nucleating materials, are used as auxiliaries to blowing agents.

Lubricants are added to plastics to promote resin fabrication and to improve properties of the final products. Compatibility with the resin most often determines which lubricant is used, although its ability to reduce melt viscosity and friction with metal surfaces is almost equally important. Compounds used as lubricants include esters, fatty acids, fatty amides, metallic stearates, waxes, fluorinated polymers, and silicones.

STABILIZERS

A large number of chemicals are used to minimize degradation of plastics by air (oxygen), heat, light, and microorganisms. Often the choice of stabilizer depends on the anticipated end use of the plastic. Frequently, different stabilizers are combined to improve resistance of the finished plastic product to

clude the resin containing the additive, conditions and methods of processing, use of the product, and the environment in which they are used and in which they are discarded. Future government regulations are likely to have a growing influence on additive choices.

Concern over worker exposure to additives more often involves the additives themselves rather than the compounded plastics, in which the additives are encapsulated into a relatively inert polymer, the Radian

report points out. Possible hazards to workers are handled through normal safety and health procedures, most of which are those acceptable to the Occupational Safety & Health Administration, the report says. The trend toward custom compounding further reduces workplace hazards in plastics fabrication.

Coping with increasing regulations is one of the problems encountered by the several hundred companies who supply additives to the plastics industry. They also are

coping with demands by resin compounders and plastics fabricators for ever better additives that will lower cost and improve performance of their final products. To meet those concerns, the industry has ongoing developmental programs that include fundamental studies on how and why additives work, on the process of bringing new products to market, and on reformulation of existing additives.

Recent commercial developments in plastics additives are exemplified

degradation. Such combinations can impart other desirable properties to the plastic.

Antioxidants for plastics are classified as either primary or secondary. Primary antioxidants include various phenols and secondary amines that scavenge extraneous free radicals. Various phosphites and thioesters are used as secondary antioxidants (sometimes called synergists) that decompose peroxides (a source of free radicals). Many other compounds and proprietary mixtures are offered as antioxidants for plastics.

Heat stabilizers go mostly into PVC, with lesser quantities used in urethanes and some styrenics. Several of these materials also have secondary functions and may be combined with other functional compounds. Various metallic soaps, organotin, inorganic and organic lead salts, and tiny-volume specialty chemicals are used to confer heat resistance.

Light or ultraviolet stabilizers help plastics resist light degradation in several ways. Most of them absorb and/or quench the radiation. Others work similarly to antioxidants, by inactivating free radicals and peroxides. The most widely used light stabilizers are the benzophenones, which are light absorbers. Another important class of absorbers are the benzotriazoles. Organonickel compounds work as quenchers of UV light, and probably are second in use to benzophenones. A large number of other organic and inorganic compounds also are used as stabilizers.

Preservatives are used to fight microbial attack of plastics and additives such as plasticizers. Most are used in PVC, with lesser amounts in urethanes.

They are typical bacteriocides and other biocides.

PERFORMANCE ADDITIVES

Performance additives usually go into polymers during fabrication of the finished products. They account, by far, for the largest volume of plastics additives, probably more than 75% of the total. Performance additives may be put into all kinds of plastics that become finished products, but a large volume of plastics is sold without any of these additives.

Fillers and reinforcements both lower the cost of a fabricated plastic product and improve its performance, usually without any chemical reaction with the polymer. These materials range from common clays to glass fiber. The concentrations of fillers and reinforcements in plastics vary widely and may exceed 20% in some plastics.

Plasticizers rank next to fillers and reinforcements in volume consumed in plastic products. PVC accounts for 80 to 90% of the consumption of these additives. Esters of phthalic anhydride dominate use, accounting for about two thirds of the total. Other important plasticizer groups are epoxidized soybean oil esters, adipic acid esters, trimellitic anhydride esters, phosphoric acid esters, and several kinds of resins.

Colorants are chosen from a huge selection of inorganic and organic pigments. Some impart additional properties—carbon black, for example, provides stability toward light. Most colorants are supplied in concentrated form for dispersion during processing.

Impact modifiers help fabricated plastics resist fracturing when stressed. Most

have elastomeric properties. Many are acrylics or modified butadiene-styrene polymers, which usually contain acrylonitrile and methacrylate.

Flame retardants help plastics resist combustion. Various additives, especially fillers and reinforcements, affect a plastic's flame retardancy and, in turn, the amount of flame retardant needed in the plastic. There are different classes of flame-retardant additives. Inorganic compounds (particularly alumina trihydrate) are used in greater quantities than are organics such as various hydrogenated compounds and phosphorus derivatives. Some compounds, called reactive organic flame retardants, are polymerized into the resin.

Antistatic agents function by absorbing moisture from the atmosphere to provide surface moisture on plastics. The moisture dissipates the electronic charge often acquired from the atmosphere. Antistats may be added during compounding of plastics or applied after fabrication. Ethoxylated amines and quaternary ammonium salts account for most of the market, although many other chemicals are used as antistats.

Coupling agents typically are used in fabricated plastics to improve the physical bonding of fillers and reinforcements with polymers. Many different silanes are used with glass fiber and with inorganic fillers and reinforcements that contain silicon atoms. Organic titanium derivatives help bind nonsiliceous materials such as carbon black, metal oxides, calcium carbonate, and pigments to plastics. Numerous proprietary coupling agents are used in smaller quantities as binders. Many coupling agents provide various other functions.

by Ethyl's \$100 million acquisition and expansion program for its line of flame retardants. Ethyl bought the majority of the assets and technology of Dow Chemical's bromine chemical business in 1987. Now the company is building a plant to make dibromoneopentyl glycol and related materials for use in rigid and flexible polyurethane foams and unsaturated polyester resins. Other new units and expansions will provide more capacity to make complex brominated- biphenyls and

diphenoxybenzene and ethylene-(bistetrahydrophthalimide). Ethyl has other units on the drawing board to make other additives.

Another additives supplier, Ampacet, is moving into statistical process control while expanding capacity to make its line of concentrates of additives for plastics. When expansions are completed at its Terre Haute, Ind., plant, Ampacet will have capacity of 100,000 tons per year from fully automated units to make its own color concentrates and

concentrates of additives such as flame retardants, UV stabilizers, antioxidants, as well as combinations of additives and custom concentrates.

Borg-Warner Specialty Chemicals recently introduced a heat stabilizer for polyester resins and modifiers for PVC resins. The heat stabilizer is an organic diphosphite that has two functions during the melting process to fabricate the plastic for nonfiber uses. These are to deactivate catalysts remaining in polyethylene terephthalate after in-

Product Report

Overall amount of additives in plastics is declining

Millions of lb	1977	1987	1992	2000	Annual change	
					1977-87	1987-92
Fillers	3,621	5,586	6,630	8,350	4.4%	3.5%
Plasticizers	1,416	1,004	1,235	2,045	1.8	1.9
Reinforcements	615	893	1,140	1,600	3.8	5.0
Flame retardants	352	513	666	965	3.0	5.3
Colorants	276	438	525	695	4.7	3.7
Impact modifiers	57	130	180	200	6.6	4.2
Lubricants	77	96	115	150	2.2	3.7
Heat stabilizers	85	83	91	102	-0.2	1.9
UV stabilizers	4	7	9	13	5.8	5.2
Antioxidants	26	42	50	60	4.9	3.5
Organic peroxides	34	44	54	70	2.6	4.2
Chemical blowing agents	13	13	15	18	—	2.9
Antimicrobial agents	6	11	14	18	6.2	4.9
Antistatic agents	4	8	10	13	7.2	4.6
Urethane catalysts	4	6	7	9	4.1	3.1
Others	39	104	130	172	10.3	4.6
TOTAL ADDITIVES	6,663	9,664	11,450	14,480	3.8%	3.4%
TOTAL PLASTICS	30,505	49,862	61,000	80,600	5.0%	4.1%
LB OF ADDITIVES PER 100 LB OF PLASTIC	21.8	19.4	18.8	17.9		

Source: Freedonia Group

ital polymerization, and to retain color and strength properties during processing. The stabilizer also improves color and other properties of recycled polyester, according to Borg-Warner.

Borg-Warner also began offering this spring a new acrylonitrile-butadiene-styrene (ABS) impact modifier for rigid PVC and a styrene-acrylonitrile (SAN) copolymer to improve flow characteristics for the same resin during processing. The ABS impact modifier especially aids low-temperature properties of PVC, the company says. The SAN material will contribute more fluid melt to PVC without reducing basic physical properties, and it doesn't affect clarity or contribute to haze in opaque and clear thermoplastic uses, according to the company.

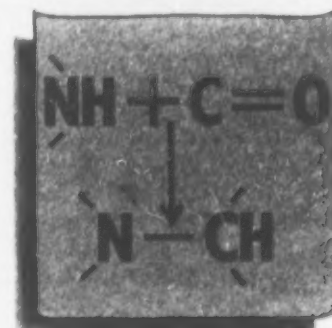
As those examples indicate, most developmental work on plastics additives is done on the chemically reactive materials. By comparison, little work on fillers and reinforcements appears to be under way, despite their large-volume use. This year, of the 10 billion lb of additives going into plastics, about three quarters will be fillers and reinforcements. Few new materials for use in those applications have been found to have better performance than the ones now used, one indus-

try source points out. Moreover, very few new fillers and reinforcements can compete cost-wise with currently used materials.

Fillers and reinforcements are used to some degree in all commercially significant resins. Loadings may vary widely, as they depend on the final makeup of the fabricated plastic product. Fabricated plastic products containing fillers and reinforcements typically use more than 20% by weight of these materials. These additives are over 90% by weight inorganic materials. Use of these materials relative to total resin consumption isn't expected to change much during the next few years, according to industry sources. Their consumption, however, will continue to grow with plastics consumption, with the rate of growth slightly lower than for all plastics.

Most fillers are used to provide bulk and lower the cost of the final product. Frequently, fillers provide other functions, such as increased weight, hardness, and chemical resistance. Some offer flame retardancy, thermal and electrical resistance, and appearance improvements. Carbon black, although accounting for only a small share of the total market for fillers, is widely used for its additional functional properties of UV light resistance,

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Product Report

insulation, and color. Calcium carbonate accounts for about half of filler consumption. Its share is forecast to decline slowly. However, it should remain the largest volume filler for a long time.

Glass fibers continue to dominate the reinforcements added to plastics, at about two thirds of the total. These fibers are available in several different forms, ranging from milled fibers to many kinds of fabrics. They account for about 15% of the total group of fillers and reinforcements added to plastics, and their share has been growing slowly, largely at the expense of asbestos.

A few exotic organic fibers and carbon fibers compete with glass fibers as reinforcements in plastics. Until costs decline further or performance improves more to justify high costs, other fibrous reinforcement materials for plastics will barely challenge the position held by glass fibers.

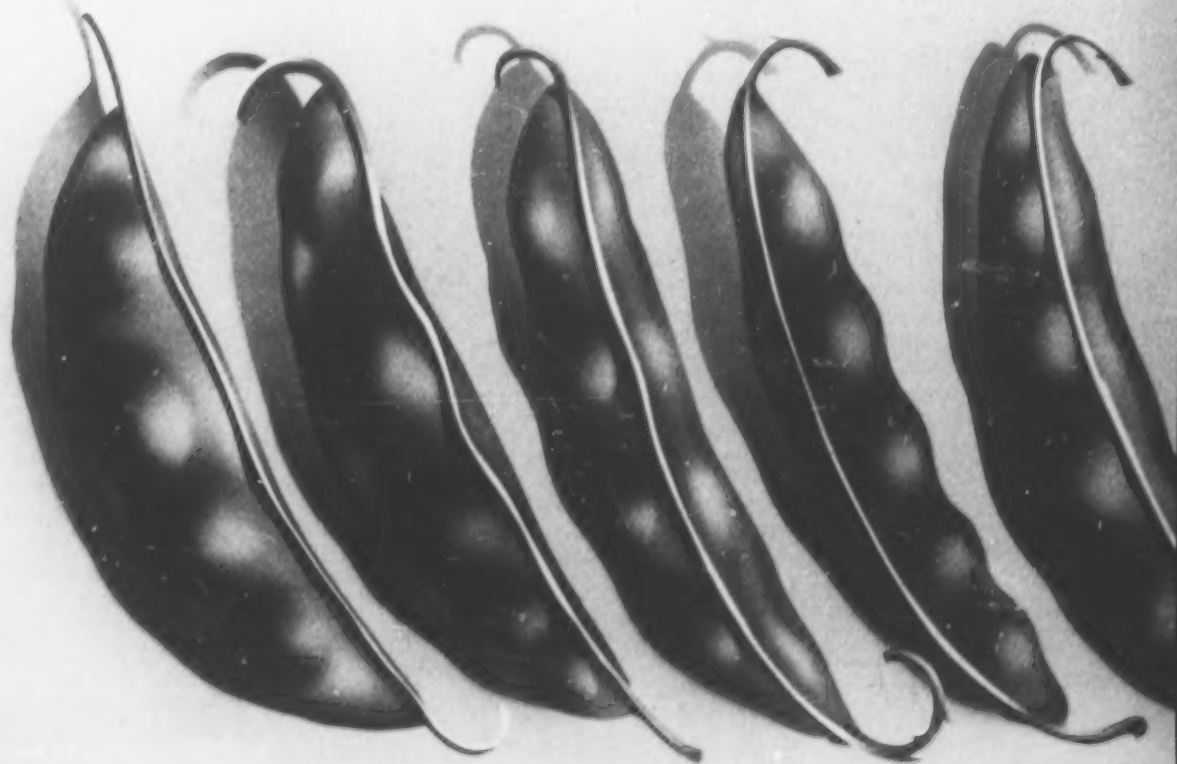
Plasticizers rank next to fillers and

reinforcements in the volume of materials consumed as additives. This year, plasticizer consumption could total more than 1.8 billion lb and exceed 2 billion lb in the early 1990s. Between 75 and 85% of plasticizer consumption is in PVC and copolymers of vinyl chloride. About half of the PVC produced contains a plasticizer. Other resins, such as polystyrene, acrylics, polyesters, polyvinyl acetate, and various thermosetting resins, sometimes utilize plasticizers in small quantities for certain end uses.

Growth in U.S. consumption of plasticizers likely will be below the average for all plastics additives or about 2.5% annually for the next few years. Part of the reason for slower growth stems from fewer new end uses being developed for vinyl plastic products that require plasticization. Another factor causing slower than average growth is the current rise in imports of fabricated vinyl plastic products.

Except for small amounts copolymerized into resins, plasticizers are compounded with finished resins and do not chemically react with the polymers. Generally, plasticizers are needed to give more flexibility to plastics. They lower the melt viscosity of the physical mixture as well as the glass transition temperature of resins. From a practical standpoint, plasticizers ease the subsequent processing of the mixture into finished products by such methods as extrusion, thermoforming, and molding.

The mechanism by which plasticizers work remains unclear. Among the possible mechanisms that have been suggested are the following: They act as a lubricant for macromolecules of resins, they reduce possible points of bonding between polymer chains, they continuously cause aggregation and deaggregation of various sized particles of resins through solvation, and they increase the free volume between resin mol-



ecules to give added flexibility. Probably a combination of these mechanisms occurs in most compounded plastics.

Most plasticizers used as plastics additives are various esters of organic acids or phosphoric acid, epoxidized soybean oil, and specialty polyesters. About two thirds of all plasticizers production in the U.S. is based on phthalic anhydride. Phthalate esters production in 1986, the latest year for which data are available, remained even with production in 1985 at 1.14 billion lb, according to the U.S. International Trade Commission. Principal alcohols combined with phthalic anhydride to make these plasticizers are 2-ethylhexyl, which gives dioctyl phthalate, and various linear alcohols in the C₆ to C₁₂ range. Some higher alcohols, often with branched chains, also are used. Selection of the alcohol for the plasticizer can be a complex process, because a range of properties can be achieved in the final fabricated

plastic product by varying the composition of the plasticizer.

Next in size to phthalate esters as plasticizers are the various epoxidized vegetable oils, of which soybean dominates. Epoxidized soybean oil plasticizers offer users relatively low cost, less migration from the plastic product, and some heat resistance, especially with some metallic derivatives added as heat stabilizers.

Several other chemicals are used as plasticizers for resins other than PVC. Besides the phosphate esters (use of these materials in plastics is small compared with other industrial uses), other commercially significant plasticizers are trimellitates, adipates, certain polyesters, and esters of many other organic acids, including citric, a specialty plasticizer for use in plastic packaging for foods.

Colorants is another large group of nonreactive plastic additives whose consumption may exceed 450

million lb in 1988, according to Freedonia Group estimates. As is the case with fillers, a large share of plastics output does not contain colorants. The number of colorants available from producers continues to grow, especially those with unusual effects such as fluorescence, phosphorescence, metallic character, and the luster and iridescent hues of pearlescence.

Despite continual work to develop new colorants, titanium dioxide and carbon black account for 80 to 90% of the colorants used in plastics. Consumption of titanium dioxide, because of its wide use in PVC pipe and fittings, siding, and other building products, is estimated to be more than three times larger than consumption of carbon black. (Use of carbon black in plastics is small compared with its use in elastomers.)

Colorant selection has been cited as one of the higher forms of the "black art" of plastics compounding.

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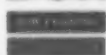
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Product Report

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Ferro	Air Products	Akzo	Ashland Chemical
Hoechst Celanese	Akzo	American Cyanamid	Cyprus Industrial
ICI Americas	BASF	BASF	Minerals
Mobay	Ciba-Geigy	Ciba-Geigy	E. C. C. America
Monsanto	Dow Chemical	Diamond Shamrock	Freeport Koalin
Olin	Du Pont	Chemicals	Great Lakes Mineral
Sandoz	Ethyl	Dow Corning	J. M. Huber
Uniroyal	Olin	Du Pont	Milwhite
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	PPG Industries	PCR Inc.	PPG Industries
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Akzo	Witco	PPG Industries	
American Cyanamid		Reichhold Chemicals	Flame retardants
Ferro	Colorants^b	Union Carbide	Aluminum Co.
Harwick Chemical	American Cyanamid	Witco	of America
Henkel	BASF		Ampacet
Hoechst Celanese	Borden Chemical	Emulsifiers	BASF
ICI Americas	Ciba-Geigy	Akzo	Dow Chemical
Lonza	Du Pont	Ashland Chemical	Ethyl
Mobay	Ferro	BASF	Ferro
Sherex	Hoechst Celanese	Ciba-Geigy	Hoechst Celanese
Witco	ICI Americas	Diamond Shamrock	M & T Chemicals
	Mobay	Chemicals	Monsanto
Blowing agents	Sandoz	Dow Chemical	Occidental Chemical
Ampacet	Sun Chemical	Du Pont	Olin
Henley Chemicals	Witco	Eastman Kodak	PPG Industries
Hoechst Celanese		C. P. Hall	Solem Industries
Mobay	Coupling agents	Hoechst Celanese	Uniroyal
Olin	Degussa	ICI Americas	Witco
Pennwalt	Dow Corning	Rohm & Haas	Heat stabilizers
Sherex	Du Pont	Union Carbide	Akzo
	Dynamit Nobel	Witco	American Cyanamid

The organic colorants, other than carbon black, are the most difficult to use, because heat, other additives, and their own physical properties can cause partial or complete loss of color during processing and subsequent possible migration to surfaces. Color concentrates, frequently containing various other plastic additives as well, are used most often in compounding.

Growth of flame retardants as plastics additives has slowed, according to recent estimates by Freedonia Group, but is forecast to increase to above the average growth rate for all additives. Flame retardant demand will exceed 525 million lb in 1988 and likely will near 1 billion lb by the year 2000.

Flame retardants may be used in most, but not all, resins. They are used to chemically and/or physically limit the combustion process by several different mechanisms. In addition, they may provide some degree of smoke suppression. The amount of inert materials used in a compounded plastic product greatly affects combustion, as do other additives that have flame retardancy as a secondary function (for example, the phosphate esters whose major function is plasticization).

Inorganic compounds, largely aluminum hydrates and metal oxides, account for more than half of the consumption of flame retardants. The next largest group is a wide variety of halogenated organic com-

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Sandoz
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Note: Representative listing of producers of some functional plastic additives. a Internal and external. b Basic only.

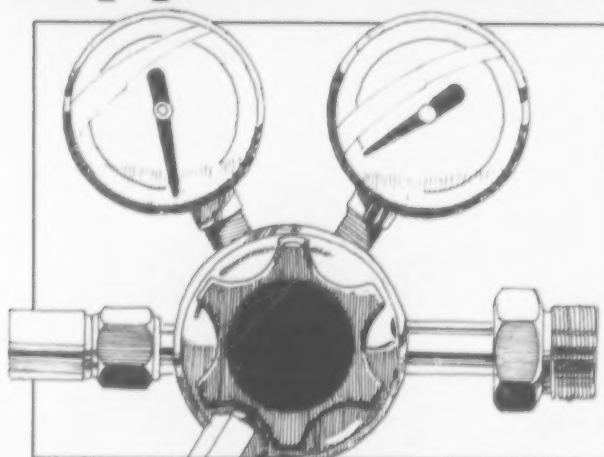
pounds. Phosphate esters, some of which are halogenated, probably are the third largest group.

Aluminum trihydrate, also used as a filler in plastics, continues to find large-volume use because of its low cost. It can be heated to decompose to the oxide, which acts as a partial heat sink, and water vapor, which dilutes the concentration of flammable materials and oxygen and also takes up heat. Much of the consumption of aluminum trihydrate is in thermoset plastic items.

Halogenated hydrocarbons, both brominated aliphatic and aromatic derivatives, find most use in polyolefins and polystyrenes. Frequently, a synergist, such as antimony oxide, iron oxides, or zinc borate,

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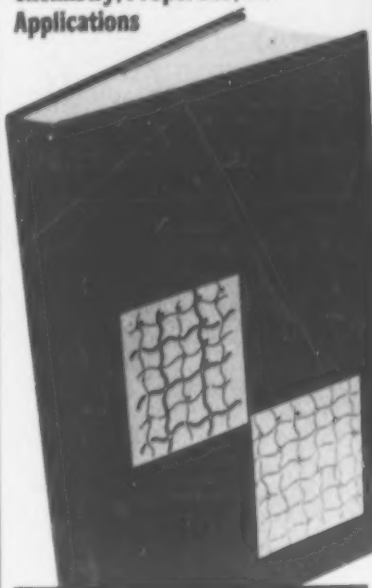
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Product Report



Additives facilitate molding of plastic amusement park cars

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Some of the halogenated hydrocarbon flame retardants, as well as some phosphorus derivatives, can be reacted with resin monomers and be made part of the polymer and distinguished as reactive flame retardants. Probably the most important use of reactive flame retardants is in epoxy resins that eventually become part of electronic components.

Phosphate esters are used as flame retardants in PVC, polyurethanes, and various engineering resins. Some are used predominately in urethanes. Phosphate esters also find significant use as plasticizers. Antimony oxide has been a strong competitor to the phosphate esters in many applications, limiting growth of the esters to well below the average growth of all flame retardants.

Impact modifiers are used largely in PVC to greatly increase resistance to stress fracturing of this resin's compounded and fabricated forms, particularly bottles, film, and sheet. Most impact modifiers are ABS or methacrylate-butadiene-styrene (MBS) polymers. Next in importance are the acrylic and modified acrylic polymers. Many other materials also are used as impact modifiers, including chlorinated polyethylene, ethylene-vinyl acetate, and various elastomers such as poly-

butadiene, ethylene-propylene-diene, and styrene-butadiene rubbers and fluoroelastomers.

The impact modifier used depends on the expected final use of the plastic part. In general, MBS is used more in products in which clarity is important, such as bottles for liquid consumer products. If the product is to be opaque, such as injection molded or sheet products, then the modifier is more likely to be ABS. For best resistance to weather—for example, vinyl siding—an acrylic polymer is favored.

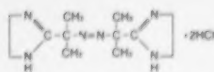
Consumption of impact modifiers for plastic products has been rising faster than consumption of all additives. This year, about 140 million lb of these elastomeric-type materials will go into plastics, with use rising to 200 million lb by 2000, forecasts Freedonia Group. Growth in use of impact modifiers is expected to continue because of the increased market for PVC bottles, credit cards, automobiles, and siding.

Lubricants as plastics additives may encompass more different compounds and proprietary products than any other functional additive class except colorants. As a result, lubricants are used in a large number of the commercially available resins. Many of the chemicals considered lubricants can have other functions when incorporated into resins. Compounding with lubri-

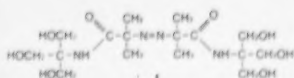
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Polymerization initiators

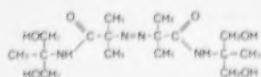
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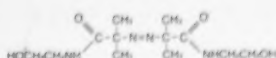
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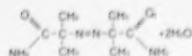
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Product Report

cants frequently can be unpredictable, according to industry sources, because of the often multifunctional characteristics of many materials used primarily as lubricants and because of their interaction with other additives going into plastics. About 100 million lb of lubricants are expected to be used in plastics this year, with growth lagging that of all additives.

Metallic soaps, mostly stearates, are the largest volume lubricant used. Combinations of these soaps can have a synergistic effect as lubricants. But besides their lubricating properties, those compounds act as mold release agents, heat stabilizers, and antiblocking agents. Use varies, depending on the metal.

Fatty acid amides rank next to metallic soaps in volume of use. These compounds provide two hydrocarbon chains linked at a polar group. As a result, they, too, have multifunctional properties, such as antiblocking and antistatic, as well as promoting flow and release of the compound from metal-forming devices.

Other materials used in significant volume as lubricants and for other functions are fatty acids and esters, fatty alcohols, paraffin and polyethylene waxes, silicones, fluoropolymers, and inorganic compounds. There is no completely reliable method for selecting the best lubricant from the long list of possible materials. Analytical methods are widely employed to attempt to predict the optimum lubricant, but the expertise of plastics compounders is required to balance the functions of lubricants and other additives if a lubricant is to be used in the processing of resins into products.

The majority of heat stabilizers used as plastics additives go into PVC and related resins. Generally, the purpose of these stabilizers is to react with hydrogen chloride released at points in PVC chains where branching or crosslinking occurs. About 85 million lb of various heat stabilizers will be consumed this year, slightly below the average annual consumption during the past 10 years. The slow decline in consumption of heat stabilizers in PVC stems from improvements in PVC

performance and a decline in fabrication of PVC in the U.S. resulting from rising imports of consumer nondurables made of PVC.

Organometallic salts account for about 40 to 50% of the consumption of heat stabilizers. The metals include barium, cadmium, calcium, zinc, potassium, and tin; the organic portion includes fatty acids, substituted phenols, and dialkyl carboxylates. Other chemicals may be combined with these compounds to act as synergists. These additives also have various secondary functions and can affect solubility of plasticizers, lubricity, and clarity.

Organotin compounds are considered to be the premium heat stabilizers because they perform well in applications where clarity and weatherability properties are important. Their cost is high, however. Various organic and inorganic lead compounds are used as heat stabilizers in PVC, largely in wire and cable insulation.

Although the need for UV stabilizers in plastics is supposedly high, consumption of these additives amounts to only about a tenth of the consumption of heat stabilizers. The relatively small volume of UV stabilizer consumption—probably about 8 million lb this year—is partly due to adequate performance of these materials at low concentrations. Limited volume of use also results from use of colorants and fillers, which provide some degree of UV protection. A third factor, and for many plastic products a critical one, is the high cost of UV stabilizers, most of which are complex organic molecules that are expensive to synthesize.

UV stabilizers operate by absorbing UV light, decomposing the peroxides that form by action of UV light, scavenging radicals that form from action of UV light (a process similar to that of antioxidation), or quenching of excited states caused by UV light. A newer class of UV stabilizers is a group of compounds known as hindered amine light stabilizers (HALS). Other classes include the benzophenones, benzotriazoles, nickelorganics, and various pigments.

Well over half of UV stabilizer consumption is in polyolefins. Fre-

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Product Report

quently, if UV stabilizers are used, combinations of a HALS and a benzophenone or a benzotriazole will be added to a polyolefin-molded item to gain synergism. Rubber-modified polystyrenes also especially benefit from use of combinations of UV stabilizers. Other resins in which UV stabilizers frequently are used include PVC, urethanes, polycarbonates, and unsaturated polyesters.

Growth in the use of antioxidants in plastics exceeds the growth of all additives, but the rate has been slowing. This year, about 45 million lb of various antioxidants will go into plastics, with consumption reaching 50 million lb in 1992, for an annual average growth rate of 3.5%, according to Freedonia Group. Although antioxidants go into most resins, their largest use is in polyolefins and polystyrenes.

Most antioxidants used in plastics are classified as either primary or secondary. Primary antioxidants,



Plastics in autos spurs market for additives, particularly impact modifiers

such as hindered phenols and secondary amines, scavenge free radicals. The secondary antioxidants—for example, phosphites and thioesters—decompose peroxides. Butylated hydroxytoluene (BHT) probably remains the most important of the hindered phenol antioxidants. How-

ever, its use has declined because of the difficulty in using it in linear low-density polyethylene, one of the faster-growing polyolefins. Even so, BHT and other hindered phenols account for about 40% of consumption.

Secondary amines have fallen into disfavor because they tend to stain plastic products. If discoloration is not a concern or is covered by colorants, these amines can be used for other functions as well as hindering oxidation.

Use of various phosphites has been growing rapidly because they work better with the HALS UV stabilizers than do the thioesters. Phosphites also have other functions as additives; they can inhibit melt index changes during processing and provide additional processing stability.

Many other kinds of plastics additives are offered, some for specific uses in certain resins and some for limited use in many different resins. Aggregate demand for all of these other additives totaled about 185 million lb in 1987, estimates Freedonia Group. The largest in consumption of these additives is the organic peroxides, followed by chemical blowing agents, antimicrobial agents, and antistatic agents.

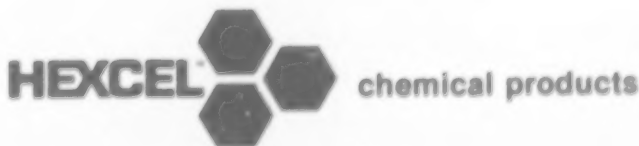
The peroxides decompose during their action and hence may not strictly be called additives, although their by-products remain. They are used mostly to cure unsaturated polyesters, to crosslink polyethylenes used as wire and cable coverings, and as initiators for polyolefins,

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PVC, polystyrene, and acrylates. A large number of different peroxides such as alkyl, aryl, and diacetyl peroxides, and peroxyesters are offered. Growth in demand for the entire group of organic peroxides used as additives trails that of all additives. Some peroxides, such as the peroxyesters, have a relatively high growth because of demand for a particular resin. But the overall growth of peroxides is offset because some will no longer be offered commercially.

Most of the blowing agents used are physical rather than chemical agents. Most physical blowing agents (90% or more of the total) are gases or volatile liquids that produce foamed plastics when pressure is reduced. The chemical blowing agents are largely hydrazine derivatives, of which azobisformamide is the most important. The materials yield nitrogen and other gases and leave various residues. Most chemical blowing agents are used in PVC and crosslinked polyethylene. About 13 million lb of chemical blowing agents are forecast to be consumed this year.

Relatively few biocides are used as plastics additives because most cannot survive the temperatures often encountered during processing. Also the cost of government registration is a factor. Those that are used go mostly into PVC and polyurethanes, with lesser amounts going into polyolefins. This year, more than 10 million lb of biocides will go into plastics, mostly as concentrates in plasticizers or solvents. Examples include organometallic compounds and nitrogen-sulfur heterocyclics, which are fungicides similar to those used in agriculture.

Use of antistatic agents this year will be less than 10 million lb, and growth exceeds that of all additives. Antistats are classified as either external or internal. External materials are used as coatings and, in a major use, are aimed at ensuring the pleasing appearance of bottles containing cosmetic, edible oils, and cleansers, by preventing deposition of dust during shipping and shelf storage. Examples of external antistats are quaternary ammonium compounds and derivatives and various ethoxylated and propoxylated aliphatics and aromatics.

Internal antistats, often supplied in an additive package containing other materials as well, are compounded into PVC, polyolefins, and polystyrene at relatively low concentrations. Those antistats move to the surface (called blooming) of the fabricated plastic item to provide a continuing function in contrast to external antistats that may be easily washed off. Ethoxylated amines are the major-volume internal antistats, and go mainly into polyolefins.

Numerous additives with special functions are available to processors. Freedonia Group estimates that demand for these additives, which include coupling agents, emulsifiers, mold release agents, slip and antiblocking agents, and viscosity depressants, will amount to about 110 million lb this year, of which 6 million lb will be catalysts for urethanes. Frequently, special functions are secondary activities of additives having more than one function.

Coupling agents act to modify surfaces of chemically inert additives such as fillers and reinforcements to help bond them to resins. Most coupling agents are silanes and titanates. Many kinds of emulsifiers are used, both in polymerization of monomers and in processing resins; other additives also may partially provide this function. Fragrances, usually added in concentrates, mask odors of plastics and other additives or provide pleasant odors for garbage bags and air fresheners. Mold release agents range from simple waxes to complex fluoroelastomers and are designed to not combine with plastics. Slip and antiblocking agents perform similar functions to mold release agents except that they are used mostly with film and with sheet forming. Viscosity depressants frequently are used in PVC plastisols as an effective substitute for plasticizers.

The current diverse and complex use of plastics additives augurs well for the continuing development of these materials in the future. Despite reduced consumption of additives per unit weight of plastic resins, the increasing number of new products being brought to market each year clearly indicates that suppliers are bullish on the outlook for plastics additives. □



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